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Decomposition of molybdate–hexamethylenetetramine complex: One single source route for different catalytic materials

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ABSTRACT

Decomposition of ammonium heptamolybdate–hexamethylentetramine (HMTA) complex $(HMTA)_2(NH_4)_4Mo_7O_{24}\cdot 2H_2O$ was studied as a function of treatment conditions in the range 300–1173 K. The evolution of solid products during decomposition was studied by thermal analysis and in situ EXAFS. Depending on the nature of the gas used for treatment, single phases of highly dispersed nitrides Mo_2N, carbide Mo_2C, or oxide MoO_2 can be obtained. The nature of the products obtained was explained by qualitative thermodynamical considerations. Morphology of the solids considerably depends on such preparation parameters as temperature and mass velocity of the gas flow. For the nitride-based materials, catalytic activity was evaluated in the model thiophene HDS reaction. It was demonstrated that NH_3-treated samples showed better catalytic activity than N_2-treated ones due to cleaner surface and better morphology. Transmission microscopy, XRD and XPS studies showed that MoS_2 is formed on the surface during HDS reaction or sulfidation with H_2S. Optimized nitride-derived catalysts showed mass activity several times higher than unsupported MoS_2 or MoS_2/Al_2O_3 reference catalyst.

1. Introduction

Transition metals nitrides and carbides are important inorganic materials with widespread range of applications, extending from superconductivity to highly resistant alloys and catalysis. Since the temperature-programmed reaction method was first applied [1–3] to synthesize unsupported Mo_2N and Mo_2C with high specific surface areas, a number of reactions including hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) [4–6], hydrogenation [7,8], ammonia synthesis [9,10] and hydrodeoxygenation [11] reactions have been studied over this type of catalysts, including monometallic or bimetallic nitrides and carbides [12]. Unsupported nitride and carbide materials as well as supported on alumina or zeolites [13] were extensively studied. To improve the textural properties of inorganic nitrides, alternative preparation methods have been proposed such as sonochemical technique [14], laser-promoted nitridation [15] or carbothermal route [16].

Recently we developed an original technique for the preparation of highly dispersed Mo_2N by decomposition of molybdate hexamethylenetetramine (HMTA) precursor [17]. HMTA molecule served at once as a source of nitrogen and as a reducing agent to remove oxygen in the form of carbon oxides. This approach was further applied to prepare bulk and supported bimetallic molybdenum nitrides with cobalt or nickel [18–20], supported nitride materials [21], metals [22] or molybdenum phosphide [23]. Though highly divided nitride was prepared by this technique, further optimization of such preparations in scope of catalytic applications was still possible. Moreover we observed that the results of preparations depend on several parameters, including the crystallinity of the precursor or the value of gas flow mass velocity. Sometimes considerable amounts of MoO_2 impurity were found in the solid products, depending on the drying conditions applied prior to the thermal treatment. Moreover, a non-intuitive dependence of the product composition on the gas composition was observed. Thus, carbide Mo_2C was observed if the reaction was carried out in hydrogen. To explain these findings and to prepare highly active unsupported catalysts, the present study has been undertaken.

2. Experimental

2.1. Preparation of solids

HMTA complex was obtained by an aqueous reaction of ammonium heptamolybdate and HMTA as described in [17]. Decomposition was carried out in a quartz reactor under nitrogen,

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ammonia or hydrogen flow, with a rate 5 K min^{-1}. In some experiments the gas flow was saturated by water vapor at 273 K (0.6 kPa pressure). The solids were kept and handled under inert atmosphere. Sulfidation was carried out in a flow of 15% H_2S/H_2 mixture at 673 K for 4 h.

2.2. *Characterizations*

X-ray diffraction patterns were obtained on a Bruker diffractometer with Cu $K\alpha$ emission. The diffractograms were analyzed using the standard ICSD files. Chemical analyses were realised using the atomic emission method. Surface areas and pore radii distributions were measured by low temperature nitrogen adsorption and calculated using BET, BJH or Horvath-Kawazoe [24] equations. The Mo content in the solids was analyzed by plasma coupled atomic emission spectroscopy (AES-ICP-Horiba Jobin Yvon). The amounts of carbon, hydrogen, nitrogen and sulfur (CHNS) in the solids were determined on a EA1110-CHNS device. Scanning electron microscopy images were obtained on a Hitachi S800 device at CMEABG center of Lyon Claude Bernard University. Transmission electron micrographs were obtained on a JEOL 2010 device with an accelerating voltage of 200 KeV. The X-ray photoelectron spectroscopy (XPS) experiments were carried out with a KRATOS AXIS Ultra DLD spectrometer using a hemispherical analyzer and working at a vacuum higher than 10^{-9} mbar. All the data were acquired using monochromatic Al $K\alpha$ X-rays (1486.6 eV, 150 W), a pass energy of 20 eV, and a hybrid lens mode. The analyzed area was 700 μm × 300 μm. Charge neutralization was carried out for all samples. The adventitious carbon (C1s = 284.5 eV) was taken as internal reference. The chemical state has been evaluated by curve fitting in the Mo 3*d*, O 1*s* and S 2*p* regions using a minimum number of doublets.

Thermal analysis experiments were carried out on a SETARAM, Setsys Evolution 12 device, coupled to a PFEIFFER Omnistar 2006 mass-spectrometer. The gaseous products evolved upon heating of the samples were studied using electron impact energy of 65 eV. The samples were heated in a platinum crucible at a rate of 5 K min^{-1} from 298 to 1173 K.

EXAFS measurements were carried out at the X1 beamline of HASYLAB synchrotron facility. In situ measurements were carried out in an in situ cell used previously in [25] and adopted from [26], represented in Fig. 1. The measurements were carried out in transmission mode at the Mo *K* edge (20,000 eV) at ambient temperature, with 2 eV step, 2 s per point. The sample thickness was chosen to give an absorption edge step of about 1.0. Phase shifts and backscattering amplitudes were obtained from FEFF [27] calculations on model compounds. The EXAFS data were treated with VIPER program [28]. Curve fitting was done alternatively in *R* and *k* space and the fit was accepted only in the case of simultaneous convergence (absolute and imaginary parts for the *R*-space). Coordination numbers (CN), interatomic distances (*R*), Debye–Waller parameters (σ^2), and energy shifts (ΔE_0) were used as fitting variables. Constraints were introduced, relating the fitting parameters in order for them to have the values lying in physically reasonable intervals. Comparison between the models depending on different number of parameters was performed on the basis of *F*-test.

2.3. *Catalytic tests*

Thiophene HDS tests were carried out without exposure to oxygen, the nitrides were prepared directly in the catalytic reactor. A weighted amount of precursor was introduced into the catalytic reactor. The precursor was decomposed under nitrogen or ammonia flow at 823–1023 K. Then the reactor was filled with argon, closed and transferred to the catalytic test and heated to 613 K with a rate 10 K min^{-1} under the flow of hydrogen saturated with thiophene. After 12 h on stream the temperature began to vary between 573 and 613 K in order to measure kinetics and to build Arrhenius's plot of the reaction rate. The properties of the solid catalysts were determined after the catalytic test. The products were analyzed using on-line gas chromatography. Reaction rate was determined using pseudo-first rate equation assuming a large excess of hydrogen and relatively low conversion (0.1 or lower).

3. Results and discussion

3.1. *Composition and properties of solid products as a function of treatment conditions*

The initial complex has chemical composition $(C_6H_{12}N_4)_2(NH_4)_4Mo_7O_{24} \cdot 2H_2O$ (**I**). This compound was precipitated and characterized earlier but we have not succeeded to grow its monocrystals suitable for structure determination. Preliminary characterizations suggested that in this compound the $Mo_7O_{24}^{6-}$ ions are preserved but NH_4^+ ions are partially substituted by protonated HTMA cations.

Decomposition of **I** under non-reactive N_2 or Ar flow led to dispersed Mo_2N, as described previously [17]. However in the course of more detailed study we observed that fine details of treatment conditions might be important. Thus, the size of crystals of **I** influences the composition of the product. Indeed, if precipitation of **I** was carried out under vigorous stirring, octahedral particles were obtained with size 10 μm (Fig. 2a), which decompose in N_2 always leading to some MoO_2 impurity. By contrast, large crystals (50 μm and more) of the same compound obtained without stirring (Fig. 2b) led to pure Mo_2N phase. This suggested that the nature of decomposition product is somewhat borderline, and even slight variations of treatment conditions are

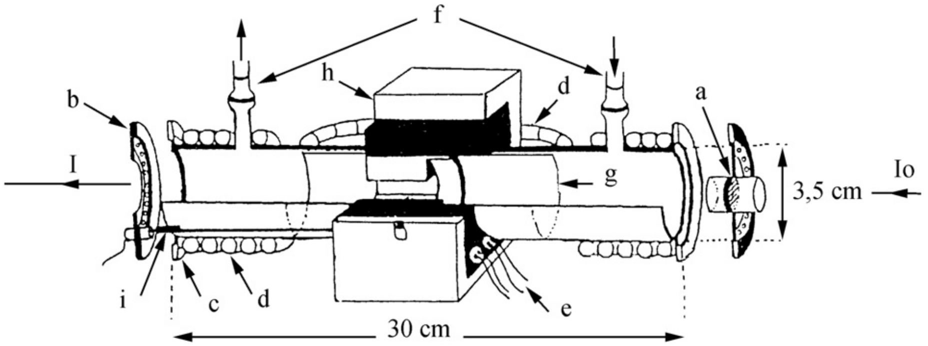

Fig. 1. In situ cell for transmission EXAFS experiments: a—quartz sample holder; b—Kapton windows; c—joints; d—cooling circuit; e—heating elements; f—gas entries; g—quartz tube; and h—furnace.